



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US96/02206 (22) International Filing Date: 16 February 1996 (16.02.96) (30) Priority Data: 08/390,726           17 February 1995 (17.02.95)    US (60) Parent Application or Grant (63) Related by Continuation US   08/390,726 (CIP) Filed on                               17 February 1995 (17.02.95) (71) Applicant (for all designated States except US): MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BRAUN, John, Ferrell [US/US]; 746 Seaclyff, Houston, TX 77062 (US). NOWAK, Robert, Thomas [US/US]; 1709 Falcon Ridge Boulevard, Friendswood, TX 77546 (US). ROOKS, Charles, Wendell [US/US]; 15330 Torrey Pines, Houston, TX 77062 (US). STEINMEYER, Daniel, Eric [US/US]; 2008 Wilson Ridge Lane, Chesterfield, MO 63005 (US).	(74) Agent: PASSLEY, Paul, Leonard; Monsanto Company, 800 North Lindbergh Boulevard, St.Louis, MO 63167 (US). (81) Designated States: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: REDUCTION OF AMMONIA WASTES ASSOCIATED WITH AMMOXIDATION PROCESSES (57) Abstract <p>Ammonia effluent from fluid bed processes for catalytic ammoxidation of propylene to form acrylonitrile are reduced by introduction of methanol into the fluid bed at selected locations.</p>		

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- 1 -

REDUCTION OF AMMONIA WASTES  
ASSOCIATED WITH AMMOXIDATION PROCESSES

**BACKGROUND OF THE INVENTION**

This application is a continuation-in-part of  
5 United States patent application serial number  
08/390,726 filed February 17, 1995 and copending  
herewith.

The invention relates to reduction of ammonia  
wastes produced in processes for production of  
10 acrylonitrile by catalytic ammoxidation of propylene in  
a fluidized bed reaction.

Commercial processes for production of  
acrylonitrile by passage of propylene, oxygen (air),  
and ammonia through a fluidized bed of ammoxidation  
15 catalyst are well known by those skilled in the art.  
In such processes an excess of ammonia is commonly  
employed and necessary to obtain high levels of  
conversion of propylene to acrylonitrile. As a result,  
significant levels of ammonia are present in the  
20 product stream and must be recovered and/or converted  
to other waste products such as ammonium nitrates or  
sulfates at considerable expense.

The addition of methanol to processes of  
catalytic ammoxidation of propylene to acrylonitrile in  
25 order to increase hydrogen cyanide co-product  
production and, to some extent, consume excess ammonia  
is known. It is further known that methanol can  
compete with propylene in ammoxidation reactions and  
difficulty may be experienced in preventing reduction  
30 in acrylonitrile yields.

It will be appreciated by those skilled in  
the art that processes for reducing ammonia wastes  
without seriously impairing conversion of propylene to  
acrylonitrile are desired from the standpoint of both  
35 economic and environmental considerations.

- 2 -

### SUMMARY OF THE INVENTION

The invention is based on the discovery that in a process for making acrylonitrile by passing propylene, oxygen (air), and ammonia through a fluidized bed of ammoxidation catalyst, the amount of ammonia contained in the product stream can be effectively and economically reduced without substantial adverse effect on acrylonitrile yield by introducing methanol into the reactor under non-coking conditions at a point and in an amount such that ammonia in the reactor effluent is substantially reduced without undue reduction in acrylonitrile yield. This continuation is particularly directed to the prevention of blockage of the methanol addition means used in the process. The invention will be fully understood from the following description of the preferred embodiments.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, methanol is introduced into a fluidized bed reaction system in which a bed of ammoxidation catalyst is fluidized by a flow of the reactants, propylene, ammonia, and oxygen containing gas (air). The use of such systems for the manufacture of acrylonitrile is well known.

Essentially any of the numerous catalysts known for the ammoxidation of propylene can be employed using conventional ammoxidation reaction conditions. For example, catalysts mainly consisting of bismuth phosphates or molybdates or of antimony and uranium oxides or of bismuth phosphates or molybdates doped with iron, nickel, cobalt etc., or of antimony oxide and oxides of metals such as iron, cobalt, or nickel may be used. A particularly preferred catalyst is represented by the formula  $Sb_aU_bFe_cBi_dMo_eMe_fO_g$ , in which Me is nickel or cobalt, a is 1 to 10, b is 0.1 to 5, c is 0.1 to 5, d is 0.001 to 0.1, e is 0.001 to .1, f is 0

- 3 -

to 0.1 and g is a number taken to satisfy the valences of the quantities of other components present.

Amoxidation processes using catalysts of this type are described, for example, in U.S. Patents 4,018,712,

5 4,545,943, and 4,487,850, the disclosures of these patents being incorporated herein by reference.

The methanol will be introduced at a point and in an amount such that the ammonia content of the reactor effluent will be less than 0.5 mole percent and  
10 lower than if no methanol were introduced and such that acrylonitrile production measured as weight per unit of time is at least 97% by weight of what would be obtained if no methanol were introduced. Preferably, ammonia effluent will be less than 0.25 mole percent  
15 or, most preferably, substantially eliminated with less than 1% reduction in acrylonitrile production.

In a preferred embodiment of the invention, the methanol is introduced into the fluidized bed reactor at a point where 5% to 60% by weight of the  
20 catalyst in the reactor is above the methanol introduction point. Such point can be determined by calculational methods well understood by those skilled in the fluid bed art or by actual measurement techniques based, for example, on pressure measurements  
25 made at various reactor heights. The weight of the catalyst above the injection point refers to the weight when the bed is fluidized under operating conditions. Also, it is contemplated that the catalyst charge will be an amount chosen to ensure complete amoxidation of  
30 the propylene but without undue excess. The optimum point of introduction may vary depending on how much excess catalyst, if any, is present; catalyst activity; surface area; etc. For any system, the optimum injection point can be determined by routine testing  
35 conducted in light of the disclosure herein.

The amount of methanol used will be sufficient to react with a major portion of the ammonia

- 4 -

not reacted with propylene. However it is desirable to avoid excesses of methanol which would be expensive to separate from the acrylonitrile product. Preferably, the methanol content of the effluent will be less than  
5 0.25 mole percent, most preferably, less than 0.01 mole percent. Generally, the use of from 0.8 to 2.0 times the moles stoichiometrically required to react with the ammonia in excess of that required for the ammoxidation of propylene will give satisfactory results.

10 Like the optimum point of methanol introduction, the amount of methanol to be utilized will depend upon the catalyst in use and the amount present; the quantities of other reactants present; and flow rates in the fluidized bed system. It is  
15 preferred to introduce the methanol in a downward direction so that the openings through which it is introduced will not become clogged when the reactor is shut down or methanol flow is stopped for maintenance or other reasons.

20 Since the methanol introduction means will generally be of relatively small dimensions and, more importantly, may not be operated continuously, care should be taken to prevent blockage. It is particularly preferred, in order to prevent clogging or  
25 blockage in the sparger, tube, or other means through which methanol is introduced, that a gas flow in addition to methanol be maintained at all times that a catalyst charge is present on the reactor, even if the reactor bed is not fluidized. The gas can be any inert  
30 gas which is defined as a gas which will not adversely affect the reaction or reactor materials of construction. For example, nitrogen or carbon dioxide can generally be used at any time. Air can be used in amounts which will not form explosive mixtures with  
35 methanol (or in any amount if the reactor is "down" or if methanol is not being introduced into the reaction). Steam can be conveniently and advantageously used if

- 5 -

the reaction is in progress. Mixtures of gases can be used. The gas flow linear velocity through the orifices of the methanol introduction means should exceed (preferably by ten to fifty times) the linear velocity of other gases through the fluid bed reactor. If the reactor is "down" and no gas flow, for example, from purges of the reactant inlets, is present, it is still desirable to maintain a minimal flow to ensure catalyst fines are not drawn into the methanol introduction means. It is further desirable that the openings in the sparger, tube, or other means through which methanol is introduced be significantly larger than the catalyst particles present in the reactor. More specifically, the diameters of the openings (or smallest dimension of the opening if non-round openings are used) should be at least ten, preferably, at least twenty or thirty times the mean particle size of the largest 10% by weight of the catalyst particles. There is no upper limit on opening size except such as may be dictated by considerations of gas flow patterns and rates which may also render it desirable to decrease the number of openings as opening size increases.

It is known that methanol in contact with iron or iron containing alloys or materials of construction will undergo reactions leading to coking at elevated temperatures such as commonly employed in ammoxidation reactions. In order to minimize down time for cleaning coked reactor inlet lines and spargers, it is important that the methanol be introduced under non-coking conditions. This can be accomplished by use of non-ferrous or high molybdate containing stainless steel inlet lines and spargers, but the expense may be undesirable. Alternatively, the portion of the inlet line between the reactor inlet point and point of discharge can be insulated to maintain the temperature of the conduit below coking temperature but this is frequently inconvenient and the space occupied inside

- 6 -

the reactor by an insulated conduit may interfere with fluid bed flow patterns. In accordance with the present invention, it is preferred to prevent major coking by vaporizing the methanol prior to the point  
5 the methanol inlet line enters the reactor and by locating the inlet line entry point as close to its point of discharge (the sparger) inside the reactor as possible.

In order to prevent coking, it is  
10 particularly preferred to mix the methanol with water vapor (steam) and/or air. Steam is preferred in order to prevent the possible formation of combustible or explosive mixtures. Coking can generally be adequately prevented by the use of a mixture of methanol with at  
15 least 20 mole percent steam or air or mixture thereof. The use of additional steam or air (or other gas which does not adversely affect the reaction system) may be desirable to provide a volume of gas flow sufficient to assure good distribution of the methanol in the fluid  
20 bed system. However, the amount of air, if any, mixed with the methanol should not be so great as to form a flammable mixture.

Minor modifications in the primary acrylonitrile process may be desirable to optimize  
25 production of acrylonitrile and, if desired, co-products such as hydrogen cyanide. Better hydrogen cyanide yields and less loss of acrylonitrile are experienced if the oxygen (air) to propylene ratio is increased so that the oxygen exiting the reaction is  
30 about the same as in the case of the conventional (no methanol present) process for ammoxidation of propylene. The oxygen (air) should be sufficient to prevent catalyst reduction but not so great as to form explosive mixtures.

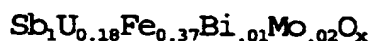
35 The practice of the invention and its comparison with conventional processes is further illustrated by the following examples.



- 7 -

## EXAMPLES I-XVII

In these examples, a 4.1 cm inside diameter by 1.8 meter high fluidized bed reactor constructed of 316 stainless steel is used. The outlet end of the reactor is connected to a gas chromatograph for analysis of effluent gases. Propylene, ammonia and air feeds are supplied via mass flow controllers and are premixed before being brought into contact with the fluidized bed. The methanol is fed separately by a positive displacement pump and is vaporized by heating prior to being introduced into the reactor. The reactor contains the amount shown in Table 1 below of catalyst indicated. Catalyst number 1 has the following composition:



(O<sub>x</sub> indicates the elements are present as their oxides and the composition contains sufficient oxygen to satisfy their valences) which is deposited on 50% by weight SiO<sub>2</sub> carrier. Catalyst 2 is a mixture of iron and antimony oxides deposited on a silica carrier. Catalyst 3 is a mixture of bismuth, molybdenum, and iron oxides on a silica carrier.

Since catalyst activity may vary somewhat with extended usage, each example compares a limited number of successive runs with methanol in the feed stream against a control in which no methanol is introduced.

In all cases, an inert gas flow through the methanol sparger openings (which are about thirty times the diameter of the mean particle size of the largest 10% by weight of the catalyst particles) at a linear velocity about 30 times greater than the linear velocity of the flow of other gases through the reactor is maintained. No clogging of the sparger is observed.

No coking is observed in the examples.

TABLE 1

		Example I		Example II	
<b>CATALYST:</b>		1	1	1	1
<b>REACTOR CONDITIONS :</b>					
REACTOR TEMP	deg C	458	458	459	459
REACTOR PRESS	atms	2.02	2.02	2.02	2.01
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91		3.91
CATALYST CHARGE	gms	340	340	340	340
<b>REACTOR FEEDS :</b>					
NH3 FEED	MOL/HR	1.427	1.427	1.419	1.419
C3H8 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	14.25	14.249	14.243	14.243
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.193		0.152
NH3/C3H8 FEED	RATIO	1.098	1.098	1.092	1.092
AIR/C3H8 FEED	RATIO	10.967	10.966	10.961	10.961
MeOH/C3H8 FEED	RATIO		0.148		0.117
<b>EFFLUENT CONDITIONS :</b>					
MOLE % NH3 in EFFLUENT		0.558	0.156	0.450	0.274
MOLE % O2 in EFFLUENT		3.056	2.640	3.334	3.231
MOLES METHANOL OUT			0.085		0.091
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.90		1.85
PROPYLENE CONVERSION	mole %	98.751	98.207	98.487	97.904
METHANOL CONVERSION	mole %		56.171		40.253
<b>PRODUCT RESULTS and RESULTS :</b>					
AN MAKE	gms/hr	56.378	56.810	56.444	57.327
HCN MAKE	gms/hr	6.891	7.198	6.461	7.238
RATIO HCN /AN	gms HCN/gm AN	0.122	0.127	0.114	0.126
NH3 Breakthrough	gms/hr	1.729	0.492	1.393	0.861
NH3 Reduction	gms/hr		1.237		0.532

TABLE 1

		Example III		Example IV	
<b>CATALYST:</b>		1	1	1	1
<b>REACTOR CONDITIONS :</b>					
REACTOR TEMP	deg C	459	459	457	457
REACTOR PRESS	atmos	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	33.02	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91		24.29
CATALYST CHARGE	gms	340	340	340	340
<b>REACTOR FEEDS :</b>					
NH3 FEED	MOL/HR	1.418	1.418	1.423	1.423
C3H8 FEED	MOL/HR	1.299	1.299	1.304	1.305
AIR FEED	MOL/HR	14.242	14.243	14.24	14.244
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.152		0.169
NH3/C3H8 FEED	RATIO	1.091	1.091	1.091	1.090
AIR/C3H8 FEED	RATIO	10.961	10.961	10.917	10.912
MeOH/C3H8 FEED	RATIO		0.117		0.130
<b>EFFLUENT CONDITIONS :</b>					
MOLE % NH3 in EFFLUENT		0.422	0.143	0.474	0.112
MOLE % O2 in EFFLUENT		3.308	2.968	3.132	2.377
MOLES METHANOL OUT			0.040		0.017
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.98		1.96
PROPYLENE CONVERSION	mole %	98.265	97.452	98.284	97.243
METHANOL CONVERSION	mole %		73.824		89.740
<b>PRODUCT RESULTS and RESULTS :</b>					
AN MAKE	gms/hr	57.442	57.316	55.694	55.184
HCN MAKE	gms/hr	6.472	7.887	6.831	8.720
RATIO HCN /AN	gms HCN/gm AN	0.113	0.138	0.123	0.158
NH3 Breakthrough	gms/hr	1.306	0.449	1.469	0.353
NH3 Reduction	gms/hr		0.857		1.116

- 10 -

TABLE 1

## Example V

## CATALYST:

1	1
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## REACTOR CONDITIONS :

REACTOR TEMP	deg C	457	458
REACTOR PRESS	atms	2.02	2.01
METHANOL INJ POINT	cms	33.02	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		24.29
CATALYST CHARGE	gms	340	340

## REACTOR FEEDS :

NH3 FEED	MOL/HR	1.422	1.422
C3H8 FEED	MOL/HR	1.304	1.304
AIR FEED	MOL/HR	14.238	14.24
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387
METHANOL FEED	MOL/HR		0.189
NH3/C3H8 FEED	RATIO	1.090	1.090
AIR/C3H8 FEED	RATIO	10.916	10.917
MeOH/C3H8 FEED	RATIO		0.130

## EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.488	0.119
MOLE % O2 in EFFLUENT		2.926	2.247
MOLES METHANOL OUT			0.009
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.91
PROPYLENE CONVERSION	mole %	98.484	97.596
METHANOL CONVERSION	mole %		94.886

## PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	55.280	54.459
HCN MAKE	gms/hr	8.961	8.703
RATIO HCN /AN	gms HCN/gm AN	0.128	0.160
NH3 Breakthrough	gms/hr	1.513	0.375
NH3 Reduction	gms/hr		1.138

- 11 -

TABLE 1

## Example VI

## CATALYST:

1	1	1	1	1
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## REACTOR CONDITIONS :

REACTOR TEMP      deg C  
 REACTOR PRESS      atmos  
 METHANOL INJ POINT      cms  
 WT % of CATALYST ABOVE  
 the MeOH INJECTION PT.  
 CATALYST CHARGE      %  
                                  gms

457	457	457	457	456
2.02	2.02	2.02	2.02	2.02
41.91	41.91	41.91	41.91	41.91
	25.75	25.75	25.75	25.75
440	440	440	440	440

## REACTOR FEEDS :

NH3 FEED              MOL/HR  
 C3H6 FEED            MOL/HR  
 AIR FEED              MOL/HR  
 N2 FEED (w/MeOH)    MOL/HR  
 METHANOL FEED       MOL/HR  
 NH3/C3H6 FEED       RATIO  
 AIR/C3H6 FEED       RATIO  
 MeOH/C3H6 FEED      RATIO

1.427	1.428	1.427	1.427	1.427
1.299	1.300	1.300	1.300	1.300
14.248	14.249	14.248	14.248	14.246
0.387	0.387	0.387	0.387	0.387
	0.199	0.180	0.093	0.249
1.098	1.098	1.097	1.097	1.097
10.965	10.958	10.957	10.957	10.955
	0.153	0.115	0.071	0.182

## EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT  
 MOLE % O2 in EFFLUENT  
 MOLES METHANOL OUT  
 MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT  
 PROPYLENE CONVERSION      mole %  
 METHANOL CONVERSION       mole %

0.558	0.128	0.133	0.250	0.020
2.185	1.403	1.556	1.731	1.120
	0.002	0.001	0.001	0.003
	1.95	1.47	0.91	2.45
100.000	99.716	99.607	99.795	99.427
	99.229	99.237	99.292	98.814

## PRODUCT RESULTS and RESULTS :

AN MAKE              gms/hr  
 HCN MAKE            gms/hr  
 RATIO HCN /AN       gms HCN/gm AN  
 NH3 Breakthrough    gms/hr  
 NH3 Reduction       gms/hr

55.312	55.996	54.722	55.274	50.092
7.229	8.930	8.859	8.503	8.840
0.131	0.159	0.162	0.154	0.176
1.734	0.406	0.419	0.784	0.064
	1.328	1.315	0.950	1.670

TABLE 1

## Example VII

## CATALYST:

1	1	1
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## REACTOR CONDITIONS :

REACTOR TEMP	deg C	461	461	461
REACTOR PRESS	atms	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		14.03	14.03
CATALYST CHARGE	gms	380	380	380

## REACTOR FEEDS :

NH3 FEED	MOL/HR	1.425	1.425	1.425
C3H6 FEED	MOL/HR	1.299	1.299	1.299
AIR FEED	MOL/HR	14.258	14.257	14.259
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.159	0.319
NH3/C3H6 FEED	RATIO	1.097	1.098	1.097
AIR/C3H6 FEED	RATIO	10.977	10.975	10.978
MeOH/C3H6 FEED	RATIO		0.122	0.245

## EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.819	0.310	0.037
MOLE % O2 in EFFLUENT		3.645	2.933	2.317
MOLES METHANOL OUT			0.012	0.042
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			1.07	2.14
PROPYLENE CONVERSION	mole %	98.705	98.249	97.655
METHANOL CONVERSION	mole %		92.411	86.732

## PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.790	53.852	53.895
HCN MAKE	gms/hr	7.307	10.126	10.936
RATIO HCN /AN	gms HCN/gm AN	0.133	0.189	0.203
NH3 Breakthrough	gms/hr	2.541	0.977	0.118
NH3 Reduction	gms/hr		1.584	2.423

TABLE 1

		Example VIII			Example IX	
<b>CATALYST:</b>		1	1	1	1	1
<b>REACTOR CONDITIONS:</b>						
REACTOR TEMP	deg C	461	462	461	461	460
REACTOR PRESS	atmos	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		14.03	14.03		18.33
CATALYST CHARGE	gms	380	380	380	400	400
<b>REACTOR FEEDS:</b>						
NH3 FEED	MOL/HR	1.425	1.425	1.425	1.428	1.428
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	14.258	14.257	14.506	14.286	14.269
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.317	0.317		0.222
NH3/C3H6 FEED	RATIO	1.097	1.097	1.097	1.099	1.099
AIR/C3H6 FEED	RATIO	10.977	10.976	11.168	10.983	10.986
MeOH/C3H6 FEED	RATIO		0.244	0.244		0.171
<b>EFFLUENT CONDITIONS:</b>						
MOLE % NH3 In EFFLUENT		0.798	0.000	0.000	0.808	0.120
MOLE % O2 In EFFLUENT		3.442	2.047	2.514	2.904	2.042
MOLES METHANOL OUT			0.102	0.101		0.014
MOLES MeOH FEED / MOLE NH3 IN BC EFFLUENT			2.18	2.18		2.00
PROPYLENE CONVERSION	mole %	99.027	98.126	97.790	99.068	98.522
METHANOL CONVERSION	mole %		67.946	68.104		93.548
<b>PRODUCT RESULTS and RESULTS:</b>						
AN MAKE	gms/hr	54.496	54.158	54.079	54.783	54.166
HCN MAKE	gms/hr	7.518	10.070	10.146	7.518	9.858
RATIO HCN /AN	gms HCN/gm AN	0.138	0.186	0.188	0.137	0.182
NH3 Breakthrough	gms/hr	2.477	0.000	0.000	1.889	0.381
NH3 Reduction	gms/hr		2.477	2.477		1.506

TABLE 1

		Example X			Example XI	
<b>CATALYST:</b>		1	1	1	1	1
<b>REACTOR CONDITIONS :</b>						
REACTOR TEMP	deg C	480	481	481	480	481
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		18.33	18.33		18.33
CATALYST CHARGE	gms	400	400	400	400	400
<b>REACTOR FEEDS :</b>						
NH3 FEED	MOL/HR	1.428	1.427	1.428	1.427	1.427
C3H8 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.300
AIR FEED	MOL/HR	14.285	14.281	14.318	14.526	14.537
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.278	0.333		0.333
NH3/C3H8 FEED	RATIO	1.099	1.099	1.099	1.099	1.098
AIR/C3H8 FEED	RATIO	10.983	10.980	11.023	11.184	11.183
MeOH/C3H8 FEED	RATIO		0.214	0.257		0.256
<b>EFFLUENT CONDITIONS :</b>						
MOLE % NH3 in EFFLUENT		0.544	0.020	0.020	0.559	0.017
MOLE % O2 in EFFLUENT		2.850	1.781	1.431	2.954	1.594
MOLES METHANOL OUT			0.034	0.000		0.034
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.80	3.36		3.22
PROPYLENE CONVERSION	mole %	99.349	98.457	98.034	99.475	98.271
METHANOL CONVERSION	mole %		87.514	100.000		89.923
<b>PRODUCT RESULTS and RESULTS :</b>						
AN MAKE	gms/hr	55.336	55.782	54.818	54.808	54.545
HCN MAKE	gms/hr	7.414	9.648	10.948	7.512	10.129
RATIO HCN /AN	gms HCN/gm AN	0.134	0.173	0.200	0.137	0.186
NH3 Breakthrough	gms/hr	1.690	0.064	0.064	1.762	0.055
NH3 Reduction	gms/hr		1.626	1.626		1.707



TABLE 1

		Example XII		Example XIII		
<b>CATALYST:</b>		2	2	3	3	3
<b>REACTOR CONDITIONS :</b>						
REACTOR TEMP	deg C	451	449	460	459	459
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		43.88		28.52	26.52
CATALYST CHARGE	gms	650	650	578	578	578
<b>REACTOR FEEDS :</b>						
NH3 FEED	MOL/HR	1.359	1.360	1.562	1.562	1.562
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	15.659	15.658	13.312	13.311	13.789
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.278		0.139	0.139
NH3/C3H6 FEED	RATIO	1.046	1.047	1.203	1.203	1.203
AIR/C3H6 FEED	RATIO	12.056	12.055	10.249	10.248	10.601
MeOH/C3H6 FEED	RATIO		0.214		0.107	0.107
<b>EFFLUENT CONDITIONS :</b>						
MOLE % NH3 in EFFLUENT		0.577	0.102	0.420	0.140	0.123
MOLE % O2 in EFFLUENT		3.610	2.508	1.242	0.963	1.354
MOLES METHANOL OUT			0.025		0.010	0.023
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.47		1.89	1.89
PROPYLENE CONVERSION	mole %	88.042	97.109	98.021	98.866	98.782
METHANOL CONVERSION	mole %		90.912		92.967	83.701
<b>PRODUCT RESULTS and RESULTS :</b>						
AN MAKE	gms/hr	54.343	54.198	51.056	50.795	50.515
HCN MAKE	gms/hr	5.820	8.699	9.831	11.364	11.247
RATIO HCN /AN	gms HCN/gm AN	0.107	0.161	0.193	0.224	0.223
NH3 Breakthrough	gms/hr	1.915	0.347	1.249	0.422	0.380
NH3 Reduction	gms/hr		1.568		0.827	0.868

TABLE 1

		Example XIV		Example XV	
CATALYST:		3	3	1	1
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	459	458	460	460
REACTOR PRESS	atms	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		28.52		12.88
CATALYST CHARGE	gms	578	578	375	375
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.582	1.581	1.425	1.426
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	13.772	14.122	14.249	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.251		0.139
NH3/C3H6 FEED	RATIO	1.203	1.202	1.097	1.098
AIR/C3H6 FEED	RATIO	10.603	10.873	10.970	10.971
MeOH/C3H6 FEED	RATIO		0.193		0.107
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.400	0.000	0.412	0.091
MOLE % O2 in EFFLUENT		1.742	1.311	2.965	2.471
MOLES METHANOL OUT			0.033		0.012
MOLES MeOH FEED /MOLE NH3 in BC EFFLUENT			3.50		1.85
PROPYLENE CONVERSION	mole %	99.022	97.927	99.182	98.766
METHANOL CONVERSION	mole %		86.828		91.675
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	50.627	50.685	55.052	54.489
HCN MAKE	gms/hr	10.081	12.155	7.320	9.655
RATIO HCN /AN	gms HCN/gm AN	0.199	0.240	0.133	0.177
NH3 Breakthrough	gms/hr	1.222	0.000	1.278	0.286
NH3 Reduction	gms/hr		1.222		0.992

- 17 -

TABLE 1

## Example XVI

## CATALYST:

1	1
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## REACTOR CONDITIONS :

REACTOR TEMP	deg C	464	463
REACTOR PRESS	atms	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		12.88
CATALYST CHARGE	gms	375	375

## REACTOR FEEDS :

NH3 FEED	MOL/HR	1.426	1.426
C3H8 FEED	MOL/HR	1.299	1.299
AIR FEED	MOL/HR	14.248	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374
METHANOL FEED	MOL/HR		0.195
NH3/C3H8 FEED	RATIO	1.098	1.098
AIR/C3H8 FEED	RATIO	10.970	10.971
MeOH/C3H8 FEED	RATIO		0.150

## EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.403	0.009
MOLE % O2 in EFFLUENT		3.027	2.204
MOLES METHANOL OUT			0.026
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.65
PROPYLENE CONVERSION	mole %	99.196	98.415
METHANOL CONVERSION	mole %		86.517

## PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.223	54.047
HCN MAKE	gms/hr	7.167	9.671
RATIO HCN /AN	gms HCN/gm AN	0.133	0.175
NH3 Breakthrough	gms/hr	1.250	0.028
NH3 Reduction	gms/hr		1.222

TABLE 1

## Example XVII

## CATALYST:

1	1	1	1
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## REACTOR CONDITIONS :

REACTOR TEMP           deg C  
 REACTOR PRESS         atms  
 METHANOL INJ POINT   cms  
 WT % of CATALYST ABOVE  
 the MeOH INJECTION PT.  
 CATALYST CHARGE       gms

462	461	461	460
2.01	2.01	2.01	2.01
0.00	0.00	0.00	0.00

	100.00	100.00	100.00
400	400	400	400

## REACTOR FEEDS :

NH3 FEED               MOL/HR  
 C3H8 FEED             MOL/HR  
 AIR FEED               MOL/HR  
 N2 FEED (w/MeOH)     MOL/HR  
 METHANOL FEED        MOL/HR  
 NH3/C3H8 FEED        RATIO  
 AIR/C3H8 FEED         RATIO  
 MeOH/C3H8 FEED       RATIO

1.426	1.852	1.702	1.717
1.299	1.299	1.299	1.299
14.25	16.509	16.76	16.766
0.374	0.374	0.374	0.374
	0.503	0.503	0.503
1.098	1.272	1.310	1.322
10.971	12.710	12.904	12.908
	0.387	0.387	0.387

## EFFLUENT CONDITIONS :

MOLE % NH3 In EFFLUENT  
 MOLE % O2 In EFFLUENT  
 MOLES METHANOL OUT  
 MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT  
 PROPYLENE CONVERSION   mole %  
 METHANOL CONVERSION    mole %

0.451	0.266	0.387	0.437
3.202	2.955	3.225	3.153
	0.006	0.006	0.006
	6.12	6.12	6.12
99.084	96.848	96.813	96.943
	98.900	98.889	98.888

## PRODUCT RESULTS and RESULTS :

AN MAKE               gms/hr  
 HCN MAKE             gms/hr  
 RATIO HCN /AN       gms HCN/gm AN  
 NH3 Breakthrough     gms/hr  
 NH3 Reduction        gms/hr

55.639	54.078	54.626	54.585
8.943	15.262	15.625	15.629
0.125	0.282	0.286	0.286
1.398	0.978	1.444	1.632
	0.420	-0.045	-0.014

- 19 -

**CLAIMS:**

1. A process for making acrylonitrile by reacting propylene with ammonia and oxygen in a fluidized bed of ammoxidation catalyst said process  
5 being characterized by introducing vaporized methanol into the reactor under non-coking conditions at a point and in an amount selected such that the ammonia content of the reactor effluent is less than 0.5 mole percent and is lower than that obtained in a comparable process  
10 in which no methanol is introduced and that the acrylonitrile production is at least 97 weight percent of that obtained in a comparable process in which no methanol is introduced, an inert gas being introduced with the methanol such that total linear gas flow  
15 velocity through the orifices of the methanol introduction means exceeds the linear velocity of flow of other gases through the reactor.

2. The process of claim 1 wherein the linear velocity of gas flow through the orifices of the  
20 methanol introduction means exceeds the linear velocity of flow of other gases through the reactor by ten to thirty times.

3. The process of claim 2 in which the ammonia content of the effluent is less than 0.25 mole  
25 percent.

4. The process of claim 2 wherein acrylonitrile production is at least 99 weight percent of that obtained in a comparable process in which no  
methanol is introduced.

30 5. The process of claim 1 in which the methanol is mixed with at least 20 mole percent steam or air or mixture thereof.

6. The process of claim 5 in which the methanol is mixed with at least 20 mole percent steam.

- 20 -

7. The process of claim 6 wherein the amount of methanol introduced is controlled such that the methanol content of the effluent is less than 0.25 mole percent.

5           8. The process of claim 7 wherein the methanol content of the effluent is less than 0.01 mole percent.

9. The process of claim 5 wherein from 5 to 60 weight percent of the fluidized catalyst in the  
10 fluid bed reactor is above the methanol injection point.

10. The process of claim 1 wherein the orifices through which methanol is introduced are downwardly oriented and have least dimensions at least  
15 ten times larger than the mean particle size of the largest 10 percent by weight of the catalyst in the reactor.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/02206

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07C253/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 638 546 (STANDARD OIL CO OHIO) 15 February 1995 see claims; examples ---	1-10
X	US,A,5 288 473 (SHAW WILFRID G ET AL) 22 February 1994 see claims; examples ---	1-10
A	US,A,3 911 089 (SHIRAISHI TATSUO ET AL) 7 October 1975 see column 4, line 36 - line 49 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Int: onal Application No

PCT/US 96/02206

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